

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/01217

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 B32B5/08 B32B17/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 632 087 A (TORAY INDUSTRIES) 4 January 1995 (1995-01-04)  claims 1,2,5,6,18 page 3, column 3, line 55 -column 4, line 45 page 7, column 11, line 37 -column 12, line 46 page 8, column 14, line 50 - line 58 example 1	1-6,8, 10,12, 13,19,20
X	EP 0 488 389 A (MITSUBISHI RAYON CO) 3 June 1992 (1992-06-03) claims 1-3,6,8,9,17-19 page 3, line 31 -page 4, line 3 page 4, line 17 -page 5, line 1 page 7, line 17 - line 24 examples 1-3	1-6,8, 10,12,13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the International search

30 May 2000

Date of mailing of the International search report

07/06/2000

Name and mailing address of the ISA  
 European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Girard, S

# INTERNATIONAL SEARCH REPORT

International Application No

P 00/01217

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 257 (C-1200), 17 May 1994 (1994-05-17) & JP 06 033329 A (MITSUBISHI RAYON CO LTD), 8 February 1994 (1994-02-08) cited in the application abstract	1-6, 8, 10
A	US 5 251 414 A (DUKE DARRYL A) 12 October 1993 (1993-10-12) claims 1,3,4,6,10,11 column 4, line 24 -column 6, line 35	1-25

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P 00/01217

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0632087	A	04-01-1995	DE 69326059 D DE 69326059 T WO 9416003 A US 6027794 A	23-09-1999 27-01-2000 21-07-1994 22-02-2000
EP 0488389	A	03-06-1992	JP 4292635 A JP 4292636 A JP 4292912 A JP 4292634 A JP 4292913 A CA 2056034 A DE 69122720 D DE 69122720 T ES 2093062 T JP 5017603 A KR 9411168 B US 5279893 A	16-10-1992 16-10-1992 16-10-1992 16-10-1992 16-10-1992 30-05-1992 21-11-1996 20-03-1997 16-12-1996 26-01-1993 24-11-1994 18-01-1994
JP 06033329	A	08-02-1994	NONE	
US 5251414	A	12-10-1993	NONE	

09/1937486

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
5 October 2000 (05.10.2000)

PCT

(10) International Publication Number  
WO 00/58083 A1

(51) International Patent Classification<sup>7</sup>: B32B 5/08, 17/04

(21) International Application Number: PCT/GB00/01217

(22) International Filing Date: 30 March 2000 (30.03.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
9907204.3 30 March 1999 (30.03.1999) GB

(71) Applicants (for all designated States except US): CYTEC TECHNOLOGY CORP. [US/US]; 1105 North Market Street, Wilmington, DE 19801 (US). MATRICE MATERIAL SYSTEMS LIMITED [GB/GB]; P.O. Box 41, Poulton-le-Fylde, Lancashire FY6 8GD (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): WOOLSTEN-CROFT, David, Harold [GB/GB]; P.O. Box 41, Poulton-le-Fylde, Lancashire FY6 8GD (GB).

(74) Agent: FINDLAY, Alice, Rosemary; Lloyd Wise, Tregear & Co., Commonwealth House, 1-19 New Oxford Street, London WC1A 1LW (GB).

(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- with amended claims

(48) Date of publication of this corrected version:  
4 October 2001

(15) Information about Correction:  
see PCT Gazette No. 40/2001 of 4 October 2001, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

RECEIVED  
MAR 14 2002  
TC 1700

WO 00/58083 A1

(54) Title: COMPOSITE COMPRISING STRUCTURAL AND NON STRUCTURAL FIBERS

(57) Abstract: A composite comprises a structural component and a resin component, the structural component comprising structural fibres and a toughening additive comprising non-structural thermoplastic fibres and the resin component comprising a non-thermoplastic material. The structure component is a preform formed from the structural fibres and the thermoplastic fibres. The volume fraction of the structural fibres in the preform is at least 65 %. The composite may be produced by forming a preform from structural fibres with non-structural thermoplastic fibres to provide a structural component. Liquid resin is then injected or infused into the structural component and cured.

## COMPOSITE COMPRISING STRUCTURAL AND NON STRUCTURAL FIBERS

The present invention relates to a composite and a method of composite manufacture.

Composite materials generally comprise an array of reinforcing fibres in a resin matrix. The present global industries which utilise composite structures, for example the aerospace industry, predominantly use conventional uni-directional and fabric-based prepregs. Such prepregs are typically made by drawing continuous rovings of reinforcing fibres, or fabrics, through a bath of molten resin or resin dissolved in solvents. The prepreg is then formed into a desired shape, loaded into a mould which is closed and heated to cure the resin.

Over the last five to seven years an alternative technology for manufacturing composite parts has emerged which is generally termed liquid composite moulding. In liquid composite moulding, a dry fibrous reinforcement is loaded into a mould or tool and the resin is injected or infused into the fibres and cured.

The reinforcement is termed a "preform" which term is well known to those skilled in the art of composite as indicating an assembly of dry fibres that constitutes the reinforcement component of a composite in a form suitable for use in a liquid composite moulding process. A preform is typically an assembly of various textile forms such as fabrics, braids or mats, tailored or shaped as necessary, and is assembled as a specific operation prior to being placed into or on the mould tool.

Liquid composite moulding technologies, such as the RTM (resin transfer moulding) or vacuum infusion methods are perceived by many to be the solution to the problem of making composite parts in a number of intractable situations, such as large aerospace primary structures and high volume structural automotive components. The benefits that liquid composite moulding technologies are perceived to offer over conventional prepregs are

reduced scrap and lay-up time, non-dependence upon drape and increased shelf life properties.

However, liquid composite moulding does possess its own problems, particularly, when the end use applications require high toughness and where control of curing cycle time is critical.

Structural parts require a high degree of toughness for most applications and this is especially true of aerospace primary components. The solution to introducing high toughness in an aerospace grade composite has traditionally been to toughen the matrix – usually by the introduction of a second phase additive such as a thermoplastic polymer to the base epoxy resin matrix.

Various approaches have been employed for the addition of a thermoplastic material into the resin. The thermoplastic may be blended with the unreacted thermoset resin at elevated temperatures to produce a single phase, unreacted melt. A limitation of this approach is the level of thermoplastic that can be added to enhance toughness. As the high molecular weight thermoplastic dissolves into the resin, the viscosity of the blend rises steeply. However the very nature of the process of introducing the resin into the reinforcing fibres requires that the resins rheological properties, viscosity and elasticity are such as to allow infiltration of the resin throughout the fabric preform. This is essential if the resulting composite structure is to be free of voids and long injection times and high injection temperatures are to be avoided. Conventional toughened epoxies are extremely viscous systems which means that high pressures and massive tools are required with the necessity of heating the resins and difficulties in matching curing time and injection-fill cycles.

Thermoplastic may also be added in the form of a continuous solid film which is placed between two layers of fibre. In such processes the thermoplastic layer is generally known as the interleaf layer. A process of this type is disclosed in European Patent Application No. 0327142 which describes a composite which comprises a solid continuous layer of a

thermoplastic material placed between two layers of fibre impregnated with thermosetting resin. On heating the thermosetting layers and the interleaf layers remain as discrete layers.

A problem with the interleaf approach is that the solid thermoplastic film does not dissolve into the resin during the heat processing stage. As a result, although the final composite may show the desired increase in toughness, there is a weak resin-thermoplastic interface. The weak interface between the interlayer and matrix can cause poor resistance to cracking between plies especially when exposed to a moist environment.

Thermoplastic material may also be introduced in a powdered form. An example of this technique is disclosed in European Patent Application No. 0274899 where the thermoplastic material is either added to the resin before the prepreg is prepared or sprinkled onto the prepreg surface.

The use of powders presents a problem in that it is difficult to ensure that an even distribution of powder is supplied to the resin. There is therefore an uneven loading of the thermoplastic material with the result that the composite will have regions of different toughnesses. Furthermore, incorporation of powdered thermoplastic material in the resin is not suitable for liquid composite moulding techniques because the viscosity of the resin is increased when the particles are added to it according to standard Newtonian theory with all the consequent disadvantages as discussed above.

If the powder particles are of a similar size to the spaces between fibres, then the process of infiltration of the resin into the fibres may also result in the thermoplastic powders being filtered out leading to an agglomeration of powder where the resin enters the mould and powder free resin in the bulk of the final composite.

Whether the powdered thermoplastic is added to the resin or to the prepreg, the amount which can be incorporated is limited. Thus, so too is the

toughening effect and, in general, to achieve a reasonable improvement in toughness, expensive structural thermoplastics have to be employed.

It has been proposed, in Japanese Patent Application 6-33329, to include thermoplastic in the form of fibres. The Application discloses a reinforcement fibre mix comprising 99-80% by weight of carbon fibres or graphite fibres and 1-20% by weight of thermoplastic resin. The composite includes only uni-directional fibres and the approach is disclosed solely as useful in a classic prepreg technique.

A good composite is one having a combination of physical properties particularly suited to a specific application. The physical properties of the composite product are determined by, amongst other things, the physical properties of the solidified resin matrix material and the structural material, and the uniformity of distribution of the matrix material and the structural material in the composite. Best results are achieved where the matrix material is intimately in contact with all of the structural material.

It is therefore desirable that the resin matrix material is of such a consistency (viscosity) that it covers (wets) all of the structural material and, if necessary, fills the interstices formed in the structural material. Uniform wetting is particularly difficult to achieve where the structural material is of complex structure, for example where it is a preform, or where the ratio of the matrix material to support is particularly low.

The viscosity of the matrix material is affected by the number and types of additives. There therefore arises the problem that, although a liquid or a gel matrix material, comprising one or more additives may possess suitable physical properties when solidified, the viscosity of the liquid or gel matrix material may be too high to facilitate its even distribution around the support material, particularly where the support is complex. This results in a composite product lacking the physical characteristics expected.

Normally to achieve a good combination of properties a composite material will consist of a number of constituents. Typically for an aerospace



grade prepreg there will be a high performance fibre reinforcement combined with a complex polymeric resin matrix mix. This matrix mix normally consists of a thermosetting resin blended with various additives. These latter additives enhance the toughness of the basic resin. Such systems have complex flow characteristics and whilst they can be easily combined with fibres in a prepreg form, their use in other manufacturing techniques is limited. As for instance an attempt to use such a complex resin in an injection or resin transfer process in a complex fibre preform may result in the filtering out of additives and a non uniform product.

There is therefore a need for method of composite manufacture which overcomes the above mentioned problems particularly for large complex structures.

In accordance with a first aspect of the present invention there is provided a composite comprising a structural component and a resin component, the structural component comprising structural fibres and a toughening additive comprising non-structural thermoplastic fibres and the resin component comprising a non-thermoplastic material, and the structural component being a preform formed from the structural fibres and the thermoplastic fibres.

In accordance with a second aspect of the present invention, there is provided a structural reinforcement for use in a composite comprising a preform formed from structural fibres and non-structural thermoplastic fibres, wherein all or part of the structural fibres are combined with the non-structural thermoplastic fibres in the preform, and wherein the overall volume fraction of the structural fibres in the preform is at least 65%.

The term "structural fibre" as used herein refers to fibres which add to the strength of the ultimate composite such as glass or carbon fibres and which therefore have a modulus of elasticity greater than 50 GPa.

The term "non-structural fibre" as used herein refers to fibres which are not provided for increasing the strength of the ultimate composite as they

have a modulus of elasticity less than 20 GPa. Thus known strengthening fibres formed from materials such as Kevlar are not non-structural fibres within the terms of the present Application.

The form of the structural reinforcement enables removal of all toughening additives from the resins thus allowing use of low viscosity epoxy systems and so making impregnation of large parts feasible with sensible pressures, lightweight low cost tooling and manageable cycle times. Furthermore a significantly greater amount of toughening additive can be included without compromising any of the processability aspects of liquid composite moulding techniques.

Accordingly, in accordance with a third aspect of the present invention there is provided a method of manufacture of a composite comprising forming a preform from structural fibres with non-structural thermoplastic fibres to provide a structural component, injecting a liquid resin into the structural component, and curing the liquid resin component.

By incorporating the toughening additive into the structural component prior to addition of the resin, a lower viscosity resin may be utilised i.e. a resin substantially free of the toughening additive.

By toughening is meant the ability to increase the energy required to cause final fracture, which may manifest itself in the ability to absorb energy during impact. Such ability may be measured by suitable impact testing methods which will be known to the skilled man. Thermoplastic polymers are known to increase the ability to absorb impact energy in structural composites. By suitable formation of the preform they may be dispersed throughout the final composite to give homogenous impact resistance or introduced at specific locations to provide a zonal toughening mechanism as required in some composite parts.

Preferably, the toughening additive is a thermoplastic material whose latent heat of melting may absorb a proportion of exothermic curing energy but which, upon completion of curing, reverts to its solid form without loss of

toughening capacity. Preferably, the curing agent, resin and thermoplastic additive are selected to provide a curing step which is at least partially carried out below the melting point of the said thermoplastic additive to thereby allow absorption of some of the energy of curing in the melting or phase change of the additive should excessive exotherm occur. Preferably, the curing step is commenced below the temperature of the melting point of the additive and may go above the temperature of the melting point during the curing cycle.

Injection of low viscosity resins (heated or otherwise) can decrease the injection-fill part of the processing cycle. However, it is also necessary to decrease the cure cycle time. This could be achieved by very active resins, higher temperature etc – but the risk is always the generation of an excessive exotherm – particularly in thick parts, which would lead to a degraded or damaged final part.

Preferably, the toughening additive comprises semi-crystalline thermoplastic fibres.

A very rapid cure can be affected without risking excessive exotherms if semi-crystalline thermoplastic fibres are used as the toughening additive. Heat generated by cure at an appropriate temperature can be used to generate crystalline melting within the fibres. The latent heat of crystalline melting will then moderate the temperature rise in the thermosetting resin. The selection of toughening fibres with appropriate crystalline melting temperature allows the cure cycle to be driven to its maximum potential without risk of composite damage. The semi-crystalline fibres themselves will simply revert to their original condition on cooling and the process will not affect the ultimate toughness of the parts.

Preferred toughening additives include:- polyethylene, polypropylene, polyamides, polyethylene terephthalate, polyether-ether-ketone.

Preferably, the toughening additive is sufficient to improve the impact energy of absorption of the untoughened composite by at least 30%, most preferably, by at least 50%.

Preferably, the percentage by volume of the toughening additive in the final composite is more than 2%, more preferably, more than 5%, most preferably, more than 10%.

Preferably, the percentage by volume of the toughening additive in the final composite is not more than 30%, more preferably, not more than 25%, most preferably, not more than 20%. It is particularly preferred that the percentage toughening additive by volume in the final composite is not more than 15%.

The percentage by volume of structural fibres in the preform is preferably at least 65%. The minimum value of 65% ensures that there is sufficient structural fibres to give the required strength. Furthermore, the quantity of non-structural thermoplastic fibres in the preform is insufficient to allow direct conversion of the material into a fully consolidated thermoplastic composite by a thermal processing route. However the proportion of toughening fibres, that is, the thermoplastic fibres is high in comparison to known methods in which thermoplastic is added in particulate form and so the toughening effect is commensurately much greater than that achieved with those known methods.

Preferably, the melt temperature of the toughening additive is not the same as the curing temperature of the resin component. It can be between 80-350°C, more preferably between 100-250°C, but its final selection will depend upon the parameters of the base matrix material. Suitably it may be 20°C above the curing temperature although it has been found that with some materials, at least, it may actually be preferable for the thermoplastic fibres to melt.

The ability of the composite to be produced using a low viscosity resin will implicitly increase the rate at which a mould can be filled. However, the problem of controlling resin cure times remains. A key factor always in resin injection is ensuring that the resin fills the mould and wets the reinforcement totally before it cures. However fill time and cure time are linked and the resin

begins to cure as soon as it is mixed before injection, and this process continues throughout the injection cycle.

In a preferred embodiment, the injection and cure stages of the process are separated by removing curing agents from the resin formulation. A resin curing agent is instead added to the structural component prior to the injection of the resin component. Preferably, the curing agent is temperature activated. The curing agent may be added to the structural component by dispersion into the thermoplastic fibres.

It is now possible to obtain commercially, curing agents that are available in solid powder form and which only become active at a specific temperature. This capability particularly arises when the curing agent is encapsulated in a thermoplastic solid with a very specific melting temperature. The micronised curing agents may be dispersed in the structural reinforcement and the resin can then be injected hot without any risk of premature reaction. Resin cure can then be triggered when desired by simply raising the temperature to the critical temperature to activate the dispersed curing agents.

This embodiment allows curing of the resin prior to its addition to the structural component to be prevented. This avoids timing problems where the resin viscosity rises due to curing prior to its addition to the structural component or during the addition process. This provides a much greater degree of control over the processing and also provides more flexibility in terms of composite structures because lower viscosity resins provide less processing problems. For instance, composites with thick laminated structures may benefit whereas in prior art methods difficulties were experienced in providing sufficient resin in the middle layers and the areas of the layers furthest from the edges.

The temperature activated curing agents provide still greater control by providing the possibility of completing the resin addition prior to curing and then raising the temperature to activate curing once satisfactory mixing of resin and structural components has been accomplished. This curing

operation may be very rapid as high reactivity resins can be used and the thermoplastic fibres provide the ability to moderate an exothermic temperature rise. Furthermore it allows the possibility of improved quality assurance by enabling mould filling to be checked and rectified if in error without the concern that cure is already taking place.

Suitable resin curing temperatures, suitable curing agents for particular resins and temperatures, and melting points of thermoplastic polymers are well known to those of ordinary skill in the art.

A further preferred feature is the use of a textile veil as part of the preform by being sandwiched between layers of the structural component.

The veil, preferably has a greater absorbency rate than the structural component layer(s) either due to its thinness or the inherent absorbency or structure of the veil material or a combination of these characteristics. Accordingly, in some embodiments, it is preferred that a veil layer is provided sandwiched between the structural layers and provides means to increase the rate of infiltration of resin into the structure. Advantageously, by this means, the resin may be preferentially directed into the centre of thicker structures than has hitherto been possible.

A veil is a very fine layer of non-woven fibrous material which is typically produced by a paper making route. The veil will act to assist resin infiltration into the core of a preform by virtue of a greater resin absorbency rate than the rest of the preform. By sandwiching veils between layers of fabrics, resin may accordingly be directed into the centre of thick preforms more rapidly than has been possible hitherto. The veil will also act to provide selective toughening by being positioned at the interface between layers of fabrics which is a prime location for delamination in a composite part.

Preferably, the veil is a thin layer of fibres produced by a paper making route. Preferably, the veil is less than  $100\text{g/m}^2$ , more preferably less than  $50\text{g/m}^2$ , most preferably less than  $30\text{g/m}^2$ . The veil will provide a combination of fibre bridging with yielding and crack deflection. The veil may

also provide toughening by comprising a mixture of non-structural thermoplastic fibres and structural fibres.

Preferably the veil comprises no more than 70% non-structural thermoplastic fibres, more preferably no more than 60%. The veil may contain a minimum of 20% non-structural thermoplastic fibre. The amount of non-structural thermoplastic fibre is however determined by the need to maintain an appropriate overall structural fibre content within the preform.

The veil may also contain curing agents. If the veils are distributed throughout the preform or attached to all fabrics used in the part, then it would be possible to remove the curing agents from both the resin and from the other materials used to form the preform.

A preferred feature of such a veil is the presence of a binder material distributed on or in the veil which is, preferably, activated by the resin, preferably, by the temperature of the resin. A suitable binder is a thermoplastic with a melting point lower than that of the incoming resin. Alternatively, the resin temperature may be raised subsequent to ingress into the veil to thereby activate the binder. It is also possible to coat the binder directly onto the surface structure which is then placed between the layers of the structural component to be subsequently temperature activated but this is not as convenient as incorporating it into the veil.

In a preferred feature, the temperature of the incoming resin dissolves the binder but is not sufficient to commence curing which then takes place in a subsequent heating step. In this manner, thick sandwiched fibre fabrics and textiles may be securely bound together to form the preform prior to the curing step.

Preferably, the resin is a thermosetting resin, more preferably, an epoxy resin.

The preform may include a textile which may be a woven or non-woven fabric. The textile may comprise a hybrid yarn i.e. structural fibres and toughening fibres commingled in a hybrid yarn or the textile may comprise

structural yarn and toughening yarn mixed in a single textile. Preferably the toughening fibres are commingled with the structural fibres to form the hybrid yarn. Hybrid yarns with different ratios of non-structural thermoplastic fibres and structural fibres may be used in the same fabric or textile. Similarly hybrid yarns containing mixtures of different non-structural thermoplastic fibres and structural fibres may be used in the same fabric, textile or preform.

The basic concept of using hybrid yarns can be varied considerably. It is possible to replace all yarns in a preform with a hybrid yarn, or alternatively to replace only a section. Furthermore a large preform may consist of zones of conventional or toughened fabrics according to the needs of the part. This offers a processing advantage in that a single resin system can be used for a large part but the properties of the composite can differ in terms of toughness, and temperature capability from place to place – hence making one shot moulding of complex structures more feasible.

The properties of the composite can be varied widely by making the preform of different forms. For example, with a woven fabric the pattern in which the structural fibres and the thermoplastic fibres are provided will have an effect on the overall behaviour of the composite. The use of a structural reinforcement in the form of a textile therefore enables great versatility.

Embodiments of the present invention will now be further described with reference to the accompanying examples and drawings in which:-

Figure 1a shows a schematic laminar composite in accordance with the present invention;

Figure 1b shows the upper layer of the laminar composite of Figure 1a with a schematic impact region;

Figure 1c shows the schematic construction of the upper layer of the laminar composite of Figure 1a;

Figure 1d shows an exploded schematic view of yield zone 2 shown in Figure 1b;



Figure 2a shows a hybrid veil sandwiched between two structural layers in a laminate;

Figure 2b shows a possible construction for the hybrid veil of Figure 2a;

Figure 2c shows an alternative construction for the hybrid veil of Figure 2a;

Figure 3 shows absorbed energy versus volume fraction x thickness for various examples, and

Figures 4 to 6 show plots of impact strength as a function of thickness x volume fraction of fibres for a composite formed from glass fibres alone, Figure 4, glass fibres and polypropylene fibres, Figure 5, and glass fibres and polyamide fibres, Figure 6.

Figure 1a reveals a composite with a laminar structure of three superimposed identical flat rectangular layers: upper layer 3a; middle layer b and lower layer c. The internal structure is shown more clearly by Figure 1c which is an explosion of inset 4. The explosion shows each layer is formed from a hybrid fabric comprising yarns of structural fibre, e.g. carbon fibre interspersed with yarns of thermoplastic fibre set in a thermosetting resin matrix.

Figure 1b and Figure 1d show schematically the effect of an impact on the surface of the upper layer 3a. In particular, Figure 1b reveals a series of diagonal linear yield zones from the theoretical impact and Figure 1d shows an explosion of a linear yield zone 2 and reveals that the yield zone corresponds to a thermoplastic yarn extending in the composite layer.

Referring to Figure 2, this shows a schematic laminar composite construction similar to that of Figure 1 but with a hybrid veil sandwiched between two layers of textile. The sandwiched veil introduces toughening into the textile composite. Two alternatives of the veil construction are shown in Figures 2b and c. Figure 2b shows schematically the construction of mixed structural and non-structural fibres and thermoplastic powder whereas Figure

2c shows a singular construction of carbon fibres and thermoplastic powder. In both cases the delamination resistance and some toughening is provided by fibre bridging between the textile layers and the fibrous veil. However this is greatly enhanced by the presence of thermoplastic in the veil layer.

By appropriate design of the interply veil, the resin flow rate across the veil may be enhanced relative to the flow rate across the upper and lower structural layers and thus improve the rate of injected resin impregnation into the composite.

In both cases, the curing agent may be present with the structural components prior to the addition of the resin so that the curing process may be activated at the appropriate temperature once satisfactory "wetting" of the structural component has taken place.

#### Example 1

A composite was prepared from a fabric preform that consisted of glass fibres commingled with polypropylene fibres in a quadriaxial non crimp fabric. The fabric was impregnated with a low viscosity unsaturated polyester resin and the laminate was cured at room temperature followed by a post cure at 80°C in accordance with the resin supplier's specification.

The plate was 3 mm thick and the volume fractions of the three components as follows:-

glass fibres 0.2 v/v;

polypropylene fibres 0.2 v/v; and

polyester resin 0.6 v/v.

The laminate was subjected to a falling weight impact test to measure its energy absorption. The specific test configuration used produces absorbed energy results for glass fibre composites that fall in a master curve determined by the thickness of the laminate and the volume fraction of fibres.

The energy absorbed by the laminate prepared from the preform with polypropylene fibres added as toughening agents was 100 J.

In contrast, a similar laminate produced from identical polyester resin 0.8 v/v but reinforced with a fabric that was totally produced from glass fibres of a fibre volume fraction of 0.2 v/v and a thickness of 3 mm absorbed an average of approximately 40 J. This demonstrates that addition of the thermoplastic fibres into the preform provides a considerable toughness benefit.

### Example 2

A glass fibre epoxy composite was prepared from a DGEBA epoxy resin (diglycidyl ether of bisphenol-A cured with an amine hardener [Shell Epikote 828 cured with Ciba HY932 aromatic amine]) and a plain weave woven fabric of E-glass fibres. The fabric occupied approximately 50% by volume of the composite. A similar composite was prepared with the same level of fabric but where the fabric component contained 70% (by volume) E-glass fibres and 30% by volume of a semi-crystalline polymeric fibre, with a crystalline melting temperature of 210°C.

The composites were produced by impregnating the fabrics and laminating to a thickness of 6cm thick and cured in an oven set at 190°C. Thermocouples embedded in the centre of the laminate monitored the temperature rise in the materials as they initially equilibrated to the oven temperature and then experienced further temperature rises due to the exothermic curing process.

The laminate with just glass fibres exhibited a temperature rise well beyond the 190°C oven temperature which became rapid and reached a peak value of 300°C at which point significant degradation of the epoxy was observed. The laminate with semi-crystalline thermoplastic fibre also exhibited a temperature rise due to the exothermic cure but once this temperature reached the crystalline melting temperature of the thermoplastic

fibres, the overall temperature rise was halted and the epoxy resin did not noticeably degrade.

### Example 3

A carbon fibre composite, 3 mm thick, was prepared from a plain weave fabric and an epoxy resin (diglycidyl ether of bisphenol A cured with an amide hardener [Shell Epikote 828 cured with Ciba HY932 aromatic amine]). The fabric contained 70% by volume carbon fibres (Torayca T300) and 30% by volume nylon 6.6 fibres. The fabric was impregnated with the liquid epoxy resin and cured at room temperature for 24 hours followed by a post cure at 100°C for 4 hours. The cured laminate contained approximately 50% carbon fibres by volume and 21% of nylon fibres by volume. The remaining 29% of the composition was cured epoxy resin. A similar composite was prepared by impregnating a fabric produced exclusively from carbon fibres. In this case the plain weave carbon fibre occupied 50% of the volume of the composite and the epoxy resin matrix occupied the remaining 50%.

Both laminates were subjected to excess energy, falling weight impact tests. The laminate comprising just carbon fibres and an epoxy matrix absorbed 50 J of energy. The laminate with the carbon fibres, nylon fibres and epoxy matrix absorbed 85 J.

### Examples 4 to 7

Tests have been conducted with a series of medium volume fraction glass fibre composites which exhibit impact toughness (energy absorbed during drop weight impact with full penetration) which is enhanced by a factor of 2-3 times by inclusion of thermoplastic fibres in comparison to the unmodified analogues. Tests have also shown a remarkable lack of sensitivity to notches in open hole tension tests on the same materials.

The impact results of two materials against two control samples are shown in Figure 3 and Table 1 defines the materials tested.

Table 1

Comparison of toughened and non-toughened composite laminates.

Examples	Product	% Volume Fraction Structural Component	Structural components
Example 4	(F394)	22-23	Glass/polypropylene/ polyester
Example 5	(F404)	41	Glass/polyester
Example 6	(F384)	22-23	Glass/polypropylene/ polyester
Example 7	(F389)	25	Glass/polyester

The structural components each comprised about 50:50, glass to toughening additive, by volume.

Figure 3 shows the impact results for the Examples 4-7 as a plot of absorbed energy against thickness x volume of fibres. The impact master curve for SMC (sheet moulding composite), GMT's (glass mat thermoplastics) and prepreg etc. has been superimposed for comparative purposes. The absorbed energy for the polypropylene and polyester containing composites is significantly improved by comparison with analogous composites having no toughening additive.

Figures 4 to 6 are plots showing impact strength, that is, energy absorbed during penetration, as a function of thickness x volume fraction of fibres. Each plot has data from three different thermoset matrices – two epoxies and a polyester. The first plot of Figure 4 shows the results achieved when glass fibres alone are used with the volume fraction of glass fibres in the composite being between 30 to 50%. The second and third plots of Figures 5

and 6 show the results when the portion of the glass fibres is replaced by polypropylene, Figure 5, and polyamide, Figure 6. The plots demonstrate that the inclusion of the thermoplastic polymers provide significant benefits in terms of improved impact strength. Furthermore the effect is consistent with different matrices.

The resins used in the study which produced the plots of Figures 4 to 6 included an unsaturated isophthalic polyester resin (UP), Crystic 272 (a product of Scott Bader plc) and two epoxy systems, EP1 was a cold cure epoxy resin (diglycidyl ether of bisphenol A cured with an amide hardener (Shell Epikote 828 cured with Ciba HY932 aromatic amine) and EP2 was a low single-part, low-viscosity epoxy resin supplied by Cytec-Fiberite, Cycom 823, which was cured at 120°C.

The experimental procedure in all of these tests involved the use of an instrumented falling weight impact test in which a striker equipped with a 20 mm diameter hemispherical tip is allowed to fall onto a plate specimen of the test composite. The composite specimen is a thin plate, typically 3mm thick, and 60mm x 60 mm in size which is simply supported on a steel ring with an internal diameter of 40 mm. The striker is dropped from a height of 1m and has sufficient mass such that the kinetic energy is sufficient for the striker to completely penetrate the specimen. The test records the forces during the impact event and the energy absorbed is calculated from the force time record and the measured velocity of the striker as it impacts the specimen.

The use thermoplastic fibres incorporated into the resin matrix provides a thermoplastic region in the thermosetting matrix which gives a mechanism for plastic deformation and yielding which is not possible in the unmodified thermosetting resin on its own. The low viscosity of the unmodified thermosetting resin makes it feasible to mould large parts in reasonable time periods and to use low injection pressure for the process which will also eradicate any problems with fibre wash near the injection points due to the applied pressures.

The invention has the potential to make a number of composite fabrication techniques more effective in being able to handle a greater range of matrix formulations and their efficiency with existing systems can be increased as flow and wet out times can be reduced. This will result in a reduction in the time taken to manufacture a component.

CLAIMS

1. A composite comprising a structural component and a resin component, the structural component comprising structural fibres and a toughening additive comprising non structural thermoplastic fibres and the resin component comprising a non-thermoplastic material, and the structural component being a preform formed from the structural fibres and the thermoplastic fibres.
2. A composite as claimed in Claim 1 wherein the resin component is a thermosetting resin composition.
3. A composite as claimed in either Claim 1 or Claim 2 wherein the resin component is a low viscosity thermosetting resin composition.
4. A composite as claimed in any preceding Claim wherein the percentage by volume of the toughening additive in the composite is more than 2% but less than 30%.
5. A composite as claimed in any preceding Claim wherein the volume of the toughening additive is more than 5% but less than 25%.
6. A composite as claimed in any preceding Claim wherein the volume of the toughening additive is more than 10% but less than 20%.
7. A composite as claimed in any preceding Claim wherein the structural reinforcement component is provided in the form of a plurality of layers of textile and at least one veil is provided between a pair of adjacent layers, the veil comprising a thin layer of woven or unwoven material.
8. A composite as claimed in any preceding Claim wherein the volume fraction of the structural fibres in the preform is at least 65%.
9. Use of a structural reinforcement in the manufacture of a composite by liquid composite moulding, the structural reinforcement comprising a preform formed from structural fibres and non-structural thermoplastic fibres.



10. A structural reinforcement for use in a composite comprising a preform formed from structural fibres and non-structural thermoplastic fibres, the volume fraction of the structural fibres in the preform being at least 65%.
11. A structural reinforcement as claimed in Claim 10 wherein at least some of the thermoplastic fibres are semi-crystalline.
12. A structural reinforcement as claimed in either Claim 10 or Claim 11 further comprising a resin curing agent.
13. A structural reinforcement as claimed in Claim 12 wherein the curing agent is temperature activatable.
14. A structural reinforcement as claimed in any one of Claims 10 to 13 wherein the preform comprises layers of textile and the reinforcement component additionally includes at least one veil between an adjacent pair of layers, the veil being formed from a thin layer of woven or unwoven material.
15. A structural reinforcement as claimed in Claim 14 wherein the veil includes thermoplastic fibres.
16. A structural reinforcement as claimed in Claim 14 or Claim 15 wherein binder material is distributed on or in the veil.
17. A structural reinforcement as claimed in any one of Claims 14 to 16 wherein the veil has a greater absorbency rate for resin than the fibres.
18. A structural reinforcement as claimed in Claims 10 to 17 wherein the preform includes a textile comprising a hybrid yarn of commingled structural fibres and thermoplastic fibres or yarn of structural fibres and yarn of thermoplastic fibres.
19. A method of making a composite comprising forming a preform from structural fibres with non-structural thermoplastic fibres to provide a

structural component, injecting or infusing a liquid resin into the structural component, and curing the liquid resin component.

20. A method as claimed in Claim 19 wherein a resin curing agent is added to the structural component prior to the resin component.
21. A method as claimed in Claim 20 wherein the curing agent is encapsulated in a material which melts at a first temperature and wherein the curing step involves raising the temperature to the first temperature to activate the curing agent.
22. A method as claimed in any one of Claims 19 to 21 wherein the curing step is at least partially carried out at a temperature below the melting point of the thermoplastic fibres.
23. A method as claimed in any one of Claims 19 to 22 wherein the preform includes textile is provided in layers and a veil is provided between at least one adjacent pair of layers prior to addition of the resin, the veil comprising a thin layer of woven or non-woven material.
24. A method as claimed in Claim 23 comprising distributing binder material on or in the veil.
25. A method as claimed in any one of Claims 19 to 24 wherein the resin injection process is resin transfer moulding or composite resin injection moulding.

**AMENDED CLAIMS**

[received by the International Bureau on 7 August 2000 (07.08.00);  
original claims 1, 9, 10 and 19 amended; remaining claims unchanged (3 pages)]

1. A composite comprising a structural component and a resin component, the structural component comprising structural fibres and a toughening additive comprising non structural thermoplastic fibres and the resin component comprising a non-thermoplastic material, and the structural component being a preform comprising an assembly formed from the structural fibres and the non-structural thermoplastic fibres.
2. A composite as claimed in Claim 1 wherein the resin component is a thermosetting resin composition.
3. A composite as claimed in either Claim 1 or Claim 2 wherein the resin component is a low viscosity thermosetting resin composition.
4. A composite as claimed in any preceding Claim wherein the percentage by volume of the toughening additive in the composite is more than 2% but less than 30%.
5. A composite as claimed in any preceding Claim wherein the volume of the toughening additive is more than 5% but less than 25%.
6. A composite as claimed in any preceding Claim wherein the volume of the toughening additive is more than 10% but less than 20%.
7. A composite as claimed in any preceding Claim wherein the structural reinforcement component is provided in the form of a plurality of layers of textile and at least one veil is provided between a pair of adjacent layers, the veil comprising a thin layer of woven or unwoven material.
8. A composite as claimed in any preceding Claim wherein the volume fraction of the structural fibres in the preform is at least 65%.
9. Use of a structural reinforcement in the manufacture of a composite by liquid composite moulding, the structural reinforcement comprising a preform comprising a dry fibre assembly formed from structural fibres and non-structural thermoplastic fibres.

10. A structural reinforcement for use in a composite comprising a preform which comprises a dry fibrous assembly formed from structural fibres and non-structural thermoplastic fibres, the volume fraction of the structural fibres in the preform being at least 65%.
11. A structural reinforcement as claimed in Claim 10 wherein at least some of the thermoplastic fibres are semi-crystalline.
12. A structural reinforcement as claimed in either Claim 10 or Claim 11 further comprising a resin curing agent.
13. A structural reinforcement as claimed in Claim 12 wherein the curing agent is temperature activatable.
14. A structural reinforcement as claimed in any one of Claims 10 to 13 wherein the preform comprises layers of textile and the reinforcement component additionally includes at least one veil between an adjacent pair of layers, the veil being formed from a thin layer of woven or unwoven material.
15. A structural reinforcement as claimed in Claim 14 wherein the veil includes thermoplastic fibres.
16. A structural reinforcement as claimed in Claim 14 or Claim 15 wherein binder material is distributed on or in the veil.
17. A structural reinforcement as claimed in any one of Claims 14 to 16 wherein the veil has a greater absorbency rate for resin than the fibres.
18. A structural reinforcement as claimed in Claims 10 to 17 wherein the preform includes a textile comprising a hybrid yarn of commingled structural fibres and thermoplastic fibres or yarn of structural fibres and yarn of thermoplastic fibres.
19. A method of making a composite comprising forming a preform by combining dry structural fibres with dry non-structural thermoplastic fibres in an assembly to provide a structural component, injecting or

infusing a liquid resin into the structural component, and curing the liquid resin component.

20. A method as claimed in Claim 19 wherein a resin curing agent is added to the structural component prior to the resin component.
21. A method as claimed in Claim 20 wherein the curing agent is encapsulated in a material which melts at a first temperature and wherein the curing step involves raising the temperature to the first temperature to activate the curing agent.
22. A method as claimed in any one of Claims 19 to 21 wherein the curing step is at least partially carried out at a temperature below the melting point of the thermoplastic fibres.
23. A method as claimed in any one of Claims 19 to 22 wherein the preform includes textile is provided in layers and a veil is provided between at least one adjacent pair of layers prior to addition of the resin, the veil comprising a thin layer of woven or non-woven material.
24. A method as claimed in Claim 23 comprising distributing binder material on or in the veil.
25. A method as claimed in any one of Claims 19 to 24 wherein the resin injection process is resin transfer moulding or composite resin injection moulding.

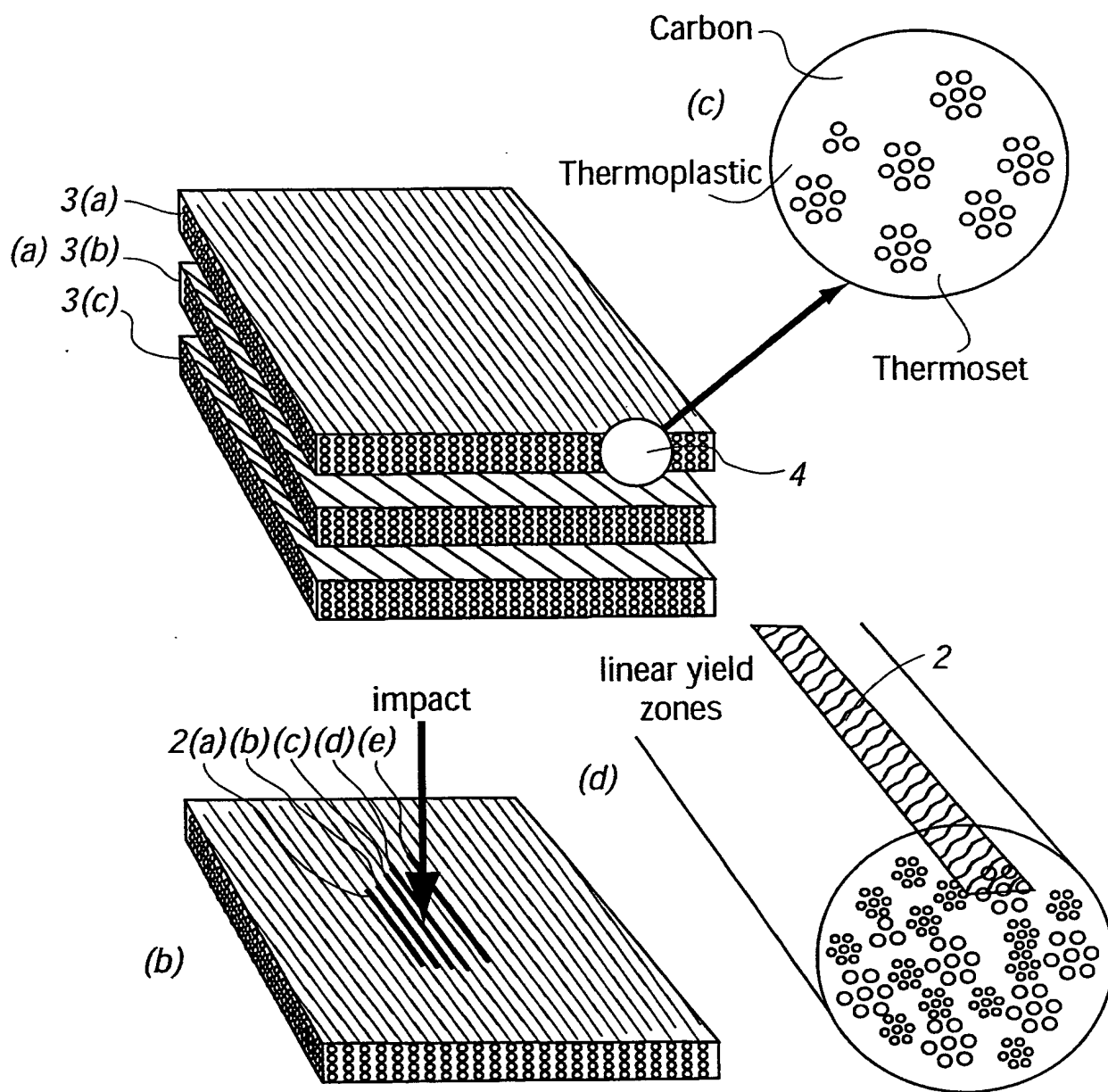


FIG. 1

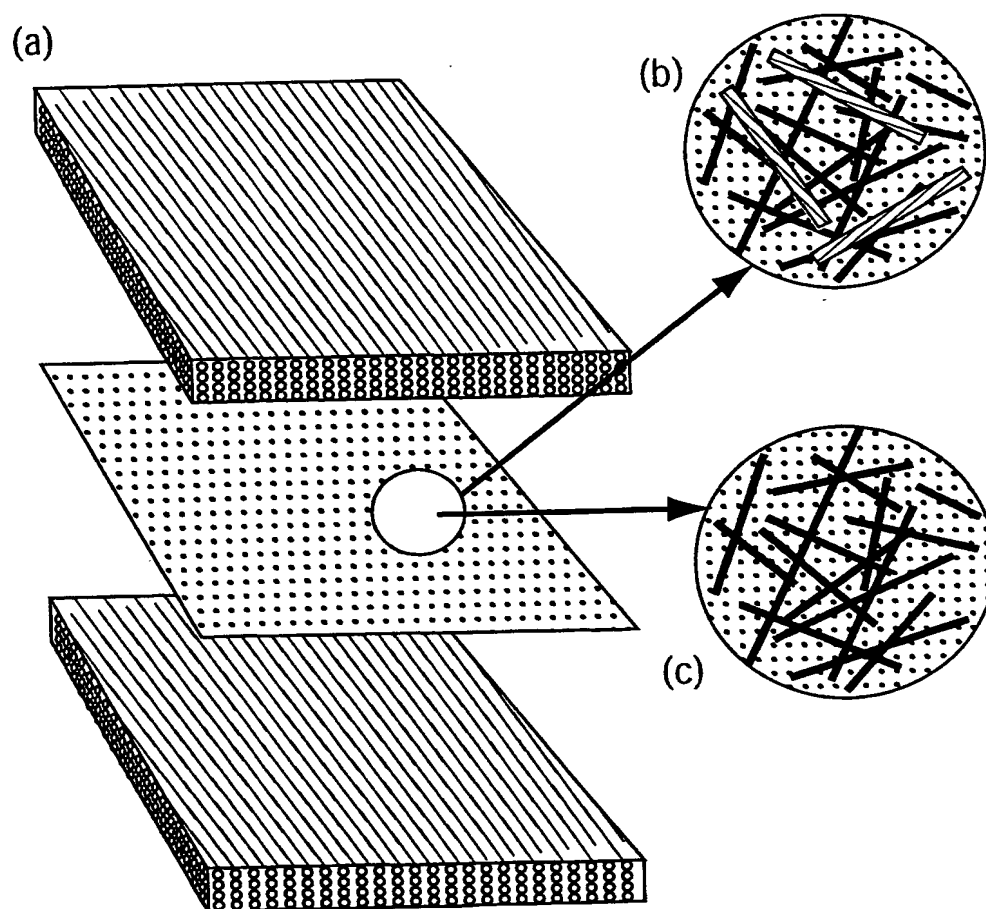
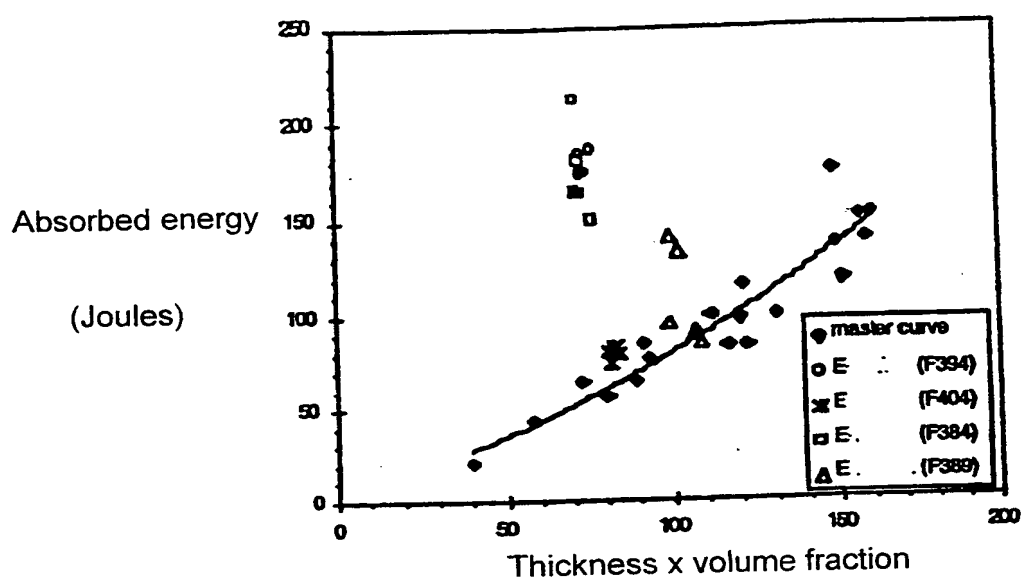
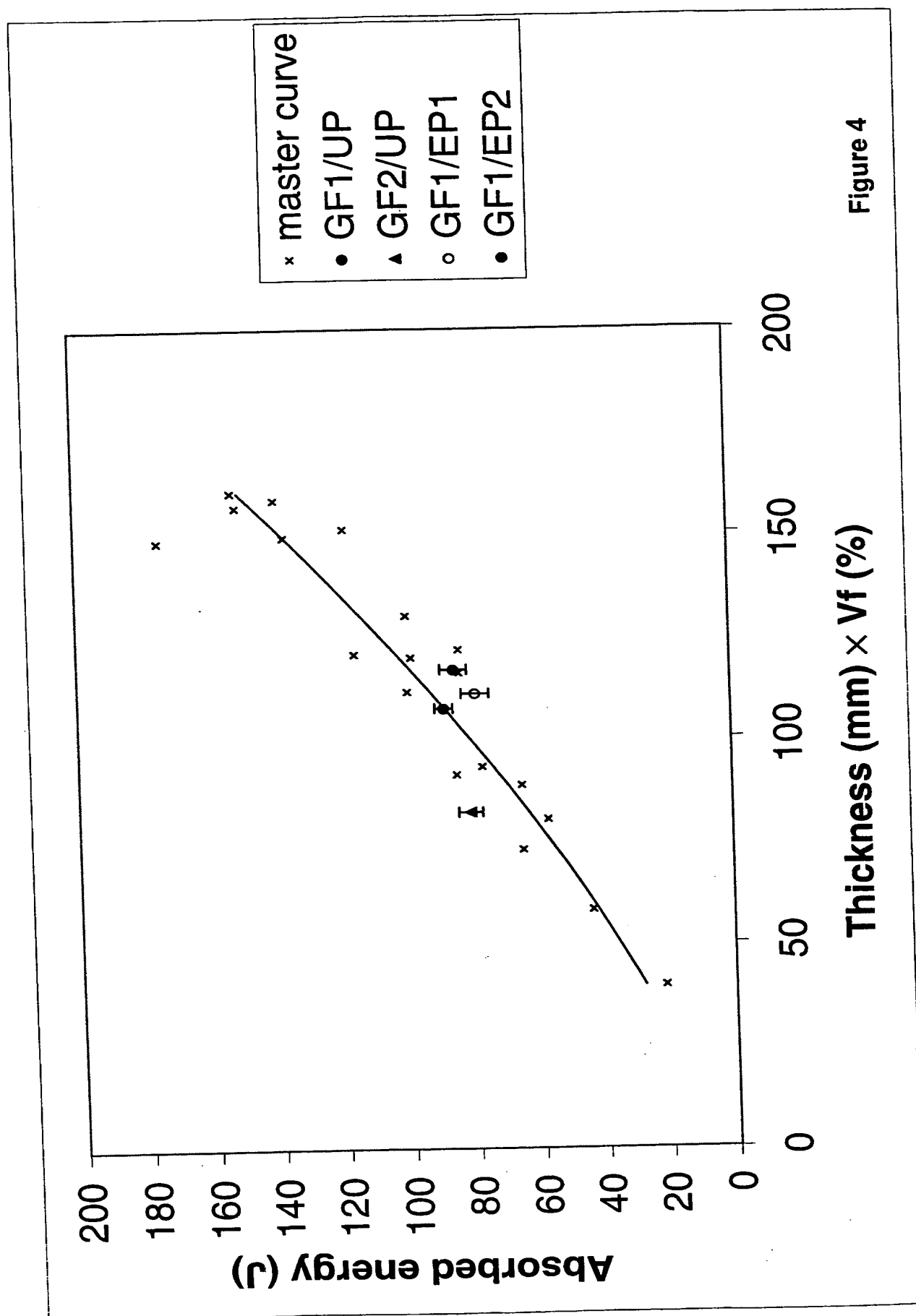
FIG. 2

Figure 3







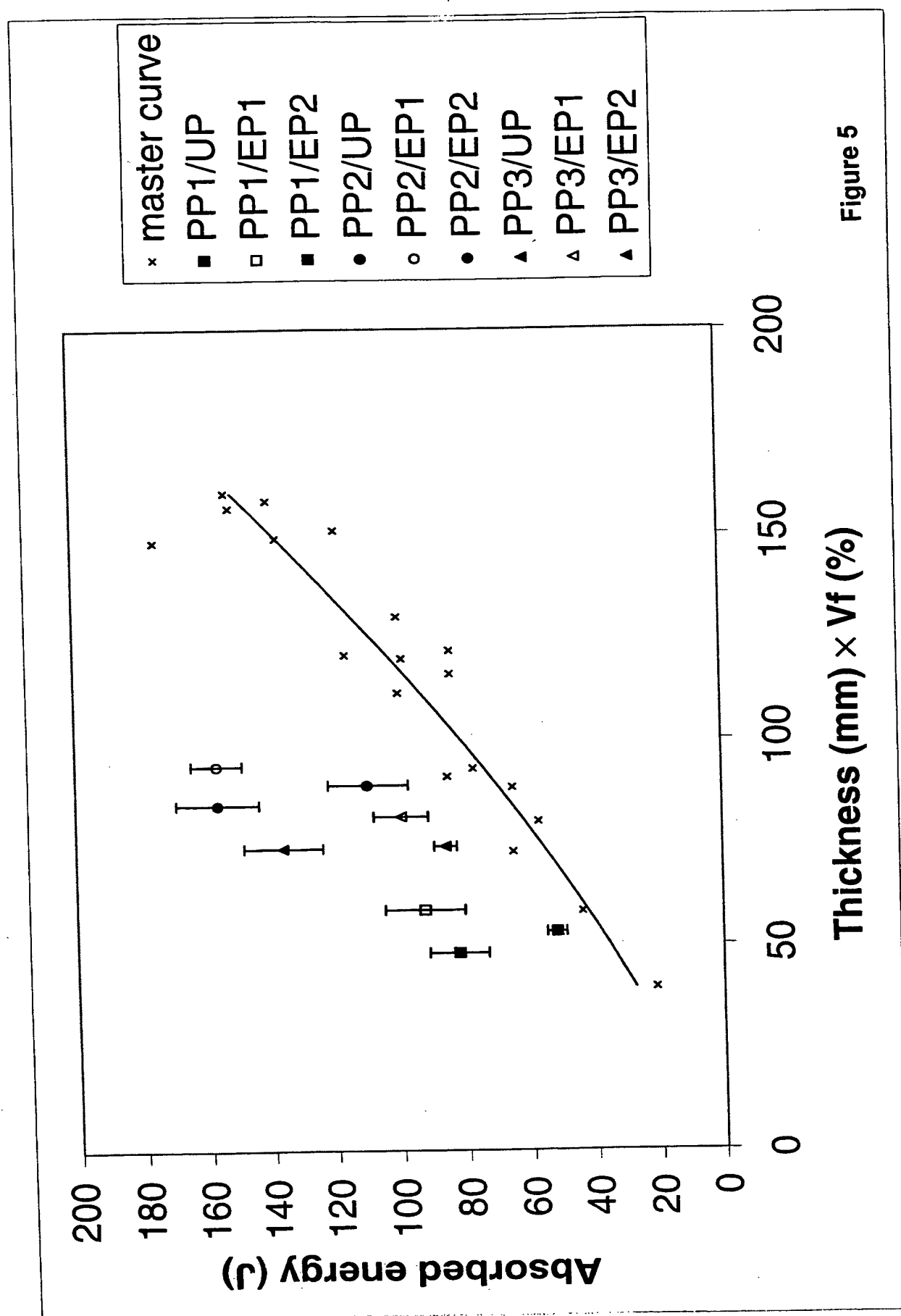


Figure 5

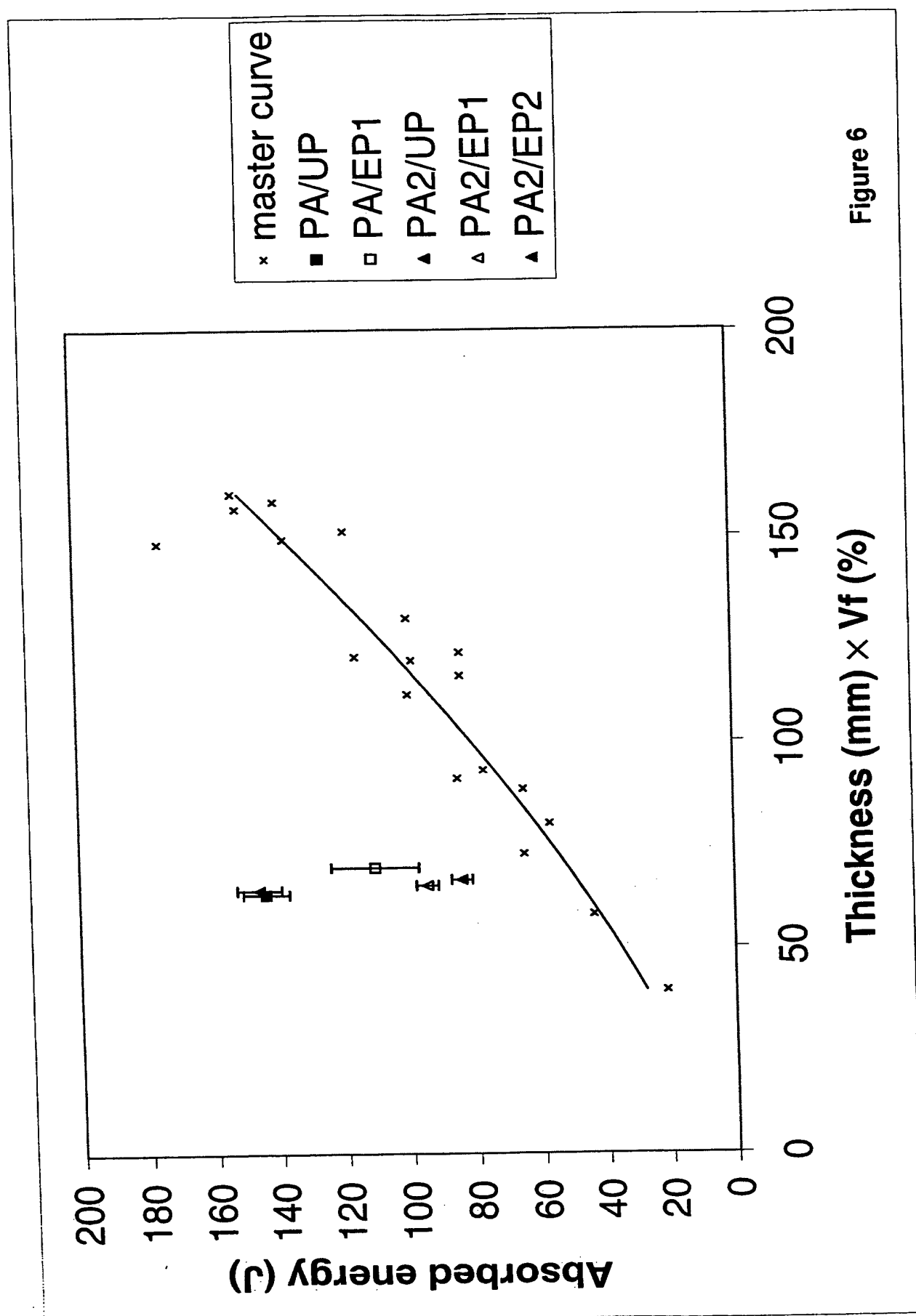


Figure 6

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01217

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B32B5/08 B32B17/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 632 087 A (TORAY INDUSTRIES) 4 January 1995 (1995-01-04)  claims 1,2,5,6,18 page 3, column 3, line 55 -column 4, line 45 page 7, column 11, line 37 -column 12, line 46 page 8, column 14, line 50 - line 58 example 1	1-6,8, 10,12, 13,19,20
X	EP 0 488 389 A (MITSUBISHI RAYON CO) 3 June 1992 (1992-06-03) claims 1-3,6,8,9,17-19 page 3, line 31 -page 4, line 3 page 4, line 17 -page 5, line 1 page 7, line 17 - line 24 examples 1-3	1-6,8, 10,12,13
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

30 May 2000

Date of mailing of the international search report

07/06/2000

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Girard, S

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/01217

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 257 (C-1200), 17 May 1994 (1994-05-17) & JP 06 033329 A (MITSUBISHI RAYON CO LTD), 8 February 1994 (1994-02-08) cited in the application abstract	1-6,8,10
A	US 5 251 414 A (DUKE DARRYL A) 12 October 1993 (1993-10-12) claims 1,3,4,6,10,11 column 4, line 24 -column 6, line 35	1-25

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/01217

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0632087 A	04-01-1995	DE 69326059 D	23-09-1999
		DE 69326059 T	27-01-2000
		WO 9416003 A	21-07-1994
		US 6027794 A	22-02-2000
EP 0488389 A	03-06-1992	JP 4292635 A	16-10-1992
		JP 4292636 A	16-10-1992
		JP 4292912 A	16-10-1992
		JP 4292634 A	16-10-1992
		JP 4292913 A	16-10-1992
		CA 2056034 A	30-05-1992
		DE 69122720 D	21-11-1996
		DE 69122720 T	20-03-1997
		ES 2093062 T	16-12-1996
		JP 5017603 A	26-01-1993
		KR 9411168 B	24-11-1994
		US 5279893 A	18-01-1994
JP 06033329 A	08-02-1994	NONE	
US 5251414 A	12-10-1993	NONE	